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(54) Process for preparing silver powder

(57) The invention is related to a process for preparing silver powder with high specific surface area, the powder obtained, the use of the powder for preparing silver containing layers and the products obtained by this use. The process comprises decomposing silvercitrate in water, a polyol or mixtures thereof, at a temperature of at least 80°C.

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Process for preparing silver powder.

The present invention is directed to a process for preparing silver powder. More in particular the invention is concerned with the production of spherical submicron silver powder.

Submicron silver particles are generally applied in the form of thick-film pastes. There are two types of thick-film pastes:

- high temperature thick-film pastes, and
- polymer thick-film paste.

The majority of the silver powders used in high temperature thick-film pastes has a spherical morphology. The pastes is applied to a ceramic substrate by screen printing. Subsequently the paste is dried and fired to remove all organic material and to obtain a sintered silver pattern.

In general there are four main routes for the production of submicron silver powder. These routes are

-reduction of Ag^+ ions with an organic reducing agent;
-reduction of Ag^+ ions with an inorganic reducing agent;
-electrodeposition; and
-plasma techniques.

The present invention is concerned with the first-mentioned main route, namely reduction of Ag^+ ions with an organic reducing agent.

An important aspect in the preparation of silver powders is the final value of the specific surface area, or, in other words, the particle size of the silver powder. For specific purposes it is preferred to prepare powders with a very high specific surface area, e.g. more than 4 m^2/g, preferably more than 6 m^2/g, more preferably more than 8 m^2/g.

In Derwent Abstract 86-112046/17 of SU-A 627,883 a process is described wherein dissolved silver nitrate was mixed with glycerol and heated at high temperature. This yields a metallic silver powder with a relatively low specific surface area.

The present invention aims at obtaining a process for preparing a silver powder with high specific surface area, and comprises decomposing silver citrate in water, in a polyol or in mixtures thereof at a temperature of at least 80°C. The process temperature is preferably between 80 and 125°C.

Surprisingly it has been found that it is possible to obtain silver powders having a high specific surface area, by the very easy method as described hereinabove.

Particularly preferred is a method, whereby silver citrate is decomposed in glycerol at a temperature of at least 100°C, preferably at about 110°C to about 120°C, whereby silver powders are obtained having a specific surface area as high as 11 m^2/g. As far as applicant is aware, such silver powders with a specific surface area of > 10.5 m^2/g are novel, and do also form part of the invention.

According to another aspect of the invention, silver citrate is decomposed in water at temperatures of 80-125°C, preferably 90-105°C, whereby silver powders are obtained having a specific surface area of 9 m^2/g.

According to another embodiment it is possible to use mixtures of polyol and water in the decomposition bath.

A particularly convenient expedient of the present invention lies therein, that by changing the time of decomposition it has become possible to obtain various values of surface area of the silver powder, without influencing the yield. For example decomposition of silver citrate in a polyol can be carried out with 100% yield in 15 minutes, giving a silver powder having a specific surface area of 11 m^2/g. Using the same reaction conditions, but with a decomposition time of 50 minutes, the specific surface area changes to 4-5 m^2/g.

The process of the present invention can be carried out by dissolving and/or suspending a suitable amount of silver citrate, such as 0.05 to 0.25 mol/l in the solvent to be used which has been preheated to the decomposition temperature. This can be water, a polyol, such as ethylene glycol or glycerol or mixtures thereof. The liquid is maintained at this temperature for the required time. The

silver powder can be filtered off and washed in a conventional manner.

In the process of the present invention it is possible to use minor amounts of co-solvents, other than those already specified, provided that these co-solvents do not interfere with the process.

During decomposition the reactor is conventionally stirred.

The silver powder thus obtained can then be mechanically comminuted into smaller agglomerates. The silver powders thus obtained are almost free of organic carbon residues and are build up of spherical primary particles with a narrow primary particle size distribution.

The silver powder can be used for preparing pastes, such as conductive thick-film pastes, which are used for preparing multilayer ceramics, ceramic capacitors, but also for conductive patterns on ceramic or polymeric substrates. In view thereof the present invention also covers the use of silver powders for preparing silver layers on various substrates, such as ceramic and polymeric materials and products thus obtained. Depending on the type of application, the applied film of silver powder containing paste is dried, and optionally sintered. This last embodiment is of course only possible when sinter resistant substrates have been used. During sintering the silver powder particles form a conductive silver layer.

Suitable high temperature thick-film paste compositions contain ethyl-cellulose, a glass-forming material, terpineol or comparable material and the silver powder, optionally in combination with other metal powders such as palladium.

The composition, which may contain other additives is prepared by mixing and/or milling the components to a paste. The paste is brought onto the surface of a substrate by suitable means, such as a screen printing apparatus.

The printed material can subsequently be dried and, depending on the use, be fired to burn the organic material of

the ink. Suitable firing temperatures are between 900 and 1100°C.

The present invention is now elucidated on the basis of some examples, which are not intended to limit the invention.

Examples 1 and 2

Silver citrate was prepared by mixing 125 ml of a 0.6 M ammonium citrate solution with 125 ml of a 1.8 M silver nitrate solution. After 5 min. reaction the slurry was filtered over a Büchner-filter and washed 3 times with water and 3 times with ethanol. The precipitate was dried during one night under vacuum at room temperature.

The silver citrate was added to glycerol preheated to 115°C in a 250 ml stirred reaction vessel in an amount corresponding to 0.065 M of Ag^+. After 10 min. the reaction was stopped. A spherical powder having a specific surface area of 11 m^2/g was obtained.

A repetition of this experiment, wherein the reaction was stopped after 60 min., gave a powder having a specific surface area of 4.5 m^2/g.

Example 3

The silver citrate was added to water preheated to 95°C in a 250 ml stirred reaction vessel in an amount corresponding to 0.065 M of Ag^+. After 10 min. the reaction was stopped. A spherical powder having a specific surface area of 6 m^2/g was obtained.

In all experiments the specific surface area was determined using nitrogen adsorption at one nitrogen partial pressure according to the method of Brunauer-Emmet-Teller, Metals Handbook, 9th Ed., Vol. 7, Powder Metallurgy, pp. 262-267.

Claims T 1128 GBR

1. Process for preparing silver powder, comprising decomposing silver citrate in water, a polyol or mixtures thereof at a temperature of at least 80°C.

2. Process according to claim 1, wherein the temperature is at most 250°C.

3. Process according to claim 1 or 2, wherein a polyol is used at a temperature of at least 100°C.

4. Process according to claims 1-3, wherein the silver citrate concentration is between 0.05 and 0.25 mol/l.

5. Process according to anyone of claims 1-4, wherein a polyol, preferably glycerol, is used.

6. Process according to claims 1-5, wherein the decomposition time is between 10 and 60 minutes.

7. Process according to claims 1-6, wherein the specific surface area of the silver powder is regulated by variation of dicomposition time.

8. Process for preparing silver powder as claimed in claim 1, substantially as described hereinbefore, especially with reference to the examples.

9. Silver powder prepared in accordance with the process of claims 1-8.

10. Silver powder having a specific surface area, as determined by N_2-adsorption, of at least 10.5 m^2/g.

11. Use of the silver powder according to claims 9 or 10 for preparing silver containing layers.

12. Use according to claim 11, for preparing conductive patterns on ceramic and polymeric substrates, and/or in ceramic capacitors.

13. Products obtained by the use of silver powder according to claim 12.

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